

Electrochemical Control of Whisker Growth on Electrodeposited Tin Coatings

A. Vincenzo and P.L. Cavallotti
Dip. Chimica Fisica Applicata
Politecnico di Milano
Via Mancinelli, 7 – 20131 Milano, ITALY
P. Crema
ST Microelectronics, Agrate (MI) - ITALY

Lead free solder finishing is an essential requirement for the new processes in electronics. Among the alternatives to Sn-Pb finish, electrodeposited (ECD) pure tin is the most reliable choice with the best set of properties. However, the use of pure tin comes up against a certain opposition, because of its tendency to spontaneously grow very fine, thread-like single crystals or whiskers.

Whisker growth on ECD Cd, Sn and Zn coatings was reported in the fifties, when it was found responsible for malfunctioning and failure of low frequency devices (1). However great the technical and scientific interest focused on this phenomenon, an exhaustive interpretation of whisker growth is still lacking.

There is substantial agreement on the primary importance of compressive stresses as driving force for whisker growth, as pointed out in early researches (2, 3). The strained material would undergo a spontaneous relaxation through complex phenomena of recovery, recrystallization and grain growth, leading to the “extrusion” of filamentary crystals. Stress may have different origin: residual stress, arisen during deposition; interfacial stress caused by the formation of intermetallic compounds (IMC); strain induced by internal stress in the substrate or by mechanical deformation. Besides the primary importance of the strain state, two other factors must be taken into account: the substrate material and the surface oxidation. As to the substrate, its influence is through IMC formation at the interface and the resulting strain effect upon the coating (4). Surface oxidation is a key factor as much important as internal stresses (5): according to Tu (6), in the absence of a uniform and tight oxide layer, stress relaxation takes place homogeneously, long-range diffusion is not activated, and whisker growth is not possible.

In this work, whisker growth is approached as a phenomenon depending on metallurgical and electrochemical factors. Starting from the above observation that, besides internal stress, the surface state plays an important role in whisker growth, as revealed by the morphological peculiarity and the extreme localisation of the phenomenon, the possibility to affect whisker growth by electrochemical treatments was investigated. According to Piontelli's classification of the electrokinetic behaviour of elements in aqueous solutions (7), tin is a normal metal: its electrochemical behaviour is characterised by low polarisation effects, both on the anodic and cathodic side, and high hydrogen overvoltage. On the other hand, the electrochemical behaviour of tin is complicated by the formation of discharge intermediates adsorbed at the surface (8) and by the presence of hydroxy-compounds which can act as surface inhibitors. On this base, we tried to promote whisker growth by modifying the surface state of the electrode through selective activation and inhibition. For this purpose it has been devised and tested a treatment with pulse reverse (PR) current on tin coatings in simple tin salt electrolytes.

Tin deposits were prepared from different commercial solutions for matt, satin-bright and bright tin plating, on different substrates: brass, hard copper, the same with a nickel layer, and Ni-Fe43% alloy, at current density in the range 50÷100mA/cm², at 40°C or room temperature. The properties of tin coatings were characterised by *in-situ* measurement of internal stress, X-ray diffraction and scanning electron microscopy (SEM). Residual stress arising during deposition were measured on brass and bronze substrate, in order to assess the relative importance of the stress factor in promoting whisker growth. Matt tin electrodeposits from acid bath at 40°C show low compressive stresses; bright tin plating solution gives coatings with only slightly higher macrostresses; in both cases, stress gradient across the thickness is zero.

The electrochemical behaviour of bulk and ECD tin electrodes was studied by polarisation measurements, chronopotentiometry and transient techniques in acidic SnSO₄ and SnCl₂ electrolytes. Based on the observed behaviour, the PR current treatment was defined and tested. Samples were treated in 0.5M SnSO₄, 1M H₂SO₄ solution, under periodic reversal polarisation with cd 1÷2 mA/cm² and zero total average current, low frequency (100÷200 ms/cycle) for 10÷30 minutes at room temperature. A few samples were immersed in the solution without current circulation. Treated and untreated specimens were held at 55°C for different times up to four months and examined periodically with optical microscope and SEM, in order to assess the effect of the PR treatment and rank different substrates and plating baths as to the susceptibility to whisker growth.

The results of this investigation show that, left unchanged the kinetics of solid state phenomena, such as dislocations motion, grain boundary migration and diffusion, the electrochemical conditioning of the surface can lower the induction period and accelerate the nucleation and/or growth of whiskers. During the PR treatment, a dynamic equilibrium is established at the electrolyte-metal interface with a micro-distribution of displacement activity at different sites on the surface. In other words, the PR treatment, as well as the simple contact with the electrolyte, is able to modify the surface of the metal through selective oxidation or inhibition and stimulation of the exchange activity at specific sites, which, upon ageing, may become preferential sites for whisker growth. Such accelerating effect is affected by many factors and further studies are required for a deeper understanding of the whole phenomenon.

References

- ¹ K.G. Kompton, A. Mendizza, S.M. Arnold, *Corrosion*, **7**, 327 (1951); E. Geoffroy, *Métaux, Corrosion, Ind.* **29**, 345 (1954) 212.
- ² R.M. Fisher, L.S. Darken, K.G. Carroll, *Acta Met.*, **2**, 370 (1954).
- ³ J. Franks, *Acta Met.*, **6**, 103 (1958).
- ⁴ K.N. Tu, *Acta Met.*, **21**, 347 (1973); U. Lindborg, *Acta Met.*, **24**, 181 (1976).
- ⁵ F.C. Frank, *Phil. Mag.*, **44**, 854 (1953).
- ⁶ K. N. Tu, *Phys. Rev. B*, **49**, 2030 (1994).
- ⁷ R. Piontelli, *J. Chim. Phys.* **46**, 288 (1949); *Z. Elektrochem.* **55**, 128 (1951).
- ⁸ Ph. Aubrun, F. Wenger, R. Wiart, *J. Appl. Electrochem.*, **7**, 225 (1977).